California Environmental Protection Agency

Air Resources Board

METHOD 310

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOC) IN CONSUMER PRODUCTS

Adopted: 9/25/97

DISCLAIMER: Mention of any trade name or commercial product in Method 310 does not constitute endorsement or recommendation of this product by the Air Resources Board.

METHOD 310
DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOC) IN CONSUMER PRODUCTS

1.0 APPLICABILITY

1.1 This method (Method 310) applies to the determination of the percent by weight of volatile organic compounds (VOC) in consumer products, antiperspirant and deodorant products, and aerosol coatings products, as defined in Title 17, California Code of Regulations, Sections 94500 *et seq*.

1.2 Method 310 determines the total volatile material in a product and the presence of any compounds prohibited by ARB regulations ("prohibited compounds"). Components of the product that do not meet the definition of a VOC or are exempted by ARB regulations for a specific product category ("exempt compounds") are subtracted from the total volatile material to determine the final VOC content for the product.

1.3 Method 310 does not apply to the determination of the composition or concentration of fragrance components or Low Vapor Pressure (LVP) compounds in products.

1.4 The term "Executive Officer" as used in this document means the Executive Officer of the Air Resources Board or his or her authorized representative.

2.0 TEST METHODS

Method 310 incorporates by reference the following American Society for Testing and Materials (ASTM), National Institute for Occupational Safety and Health (NIOSH), and United States Environmental Protection Agency (U.S. EPA) analytical test methods:

2.1 ASTM D2369-87: Standard Test Method for Volatile Content of Coatings (June 10, 1987).

2.2 ASTM D1426-93: Standard Test Methods for Ammonia Nitrogen in Water (September 15, 1993).

2.3 ASTM D4017-88: Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Titration Method (October 31, 1988).

2.4 ASTM D3792-86: Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection Into a Gas Chromatograph (November 28, 1986).

2.5 ASTM D859-88: Standard Test Method for Silica in Water (determination of polymethylsiloxanes after digestion) (August 19, 1988).

2.6 ASTM D3074-72: (Reapproved 1988) Standard Test Methods for Pressure in Metal Aerosol Containers (Approved July 28, 1972 and reapproved in 1988) with the modifications found in Appendix A.

2.7 ASTM D3063-79: (Reapproved 1984) Standard Test Methods for Pressure in Glass Aerosol Bottles (April 27, 1979 and reapproved in 1984) with the modifications found in Appendix A.

2.8 ASTM D3064-89: Standard Terminology Relating to Aerosol Products (November 24, 1989).

2.9 NIOSH: Method 1400 Alcohols I (analysis of acetone and ethanol by gas chromatography). NIOSH Manual of Analytical Methods, Volume 1 (February 1984).

2.10 U.S. EPA Method 8240, September 1986 revision 0, Gas Chromatography/Mass Spectrometry for Volatile Organics (analysis of exempt and/or prohibited compounds in the product by headspace/gas chromatography/mass spectrometry), Test Methods for Evaluating Solid Waste, Volume 1B: Laboratory Manual Physical Chemical Methods, SW-846, November 1986.

2.11 U.S. EPA Reference Method 24, Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings: 40 Code of Federal Regulations (CFR) Part 60, Appendix A, as it existed on July 1, 1994.

2.12 U.S. EPA Reference Method 24A, Determination of Volatile Matter Content and Density of Printing Inks and Related Coatings: 40 CFR Part 60, Appendix A, as it existed on July 1, 1994.

2.13 U.S. EPA Reference Methods 18, Measurement of Gaseous Organic Compound Emissions by Gas Chromatography: 40 CFR Part 60, Appendix A, as it existed on July 1, 1994.

2.14 U.S. EPA Method 300.7, March, 1986. Dissolved sodium, ammonium, potassium, and calcium in wet deposition by chemically suppressed ion chromatography.

3.0 TESTING PROCEDURE

3.1 The testing begins when the Executive Officer selects a consumer product sample for analysis by Method 310. The Executive Officer will maintain sample chain of custody throughout the selection and analytical process.

3.2. ***Initial Testing of Aerosol Products***. If the sample is an aerosol product, the aerosol propellant is separated from the liquid portion of the product by using ASTM D3074-72 (as modified in Appendix A for metal aerosol container) or ASTM D3063-79 (as modified in Appendix A for glass aerosol container). The propellant portion is analyzed for exempt or prohibited compounds by using U.S. EPA Method 18. The remaining liquid portion of the product is then analyzed as specified in section 3.3.

3.3 ***Initial Testing of Non-Aerosol Products and the Liquid Portion of Aerosol Products.*** The liquid, solid, or gel product sample is analyzed to determine the total volatile material present in the sample and to determine the presence of any exempt or prohibited compounds. This analysis is conducted by performing the following tests:[1]

3.3.1 Gravimetric analysis of samples to determine the weight percent of total volatile material, using U.S. EPA Method 24/24A, ASTM D2369-87.

3.3.2 Determination of sample water content. For determination of water content either ASTM D4017-88, or ASTM D3792-86 may be used, or results from both procedures may be averaged and that value reported.

3.3.3 Determination of ammonium content using ASTM D1426-93 or U.S. EPA Method 300.7.

3.3.4 Determination of ketones and alcohol content using NIOSH 1400.

3.3.5 Analysis of exempt and prohibited compounds, if present (U.S. EPA Method 18, U.S. EPA Method 8240, ASTM D859-88, NIOSH 1400.

3.4 ***Prohibited Compounds.*** If the sample is found to contain compounds prohibited by ARB regulations (i.e., ozone-depleting compounds) at concentrations equal to or exceeding 0.1 percent by weight, the Executive Officer will reanalyze the sample for confirmation.

3.5 ***Initial Determination of VOC Content.*** The Executive Officer will determine the VOC content pursuant to sections 3.2 and 3.3. Only those components with concentrations equal to or greater than 0.1 percent by weight will be reported.

3.5.1 Using the appropriate formula specified in section 4.0, the Executive Officer will make an initial determination of whether the product meets the applicable VOC standards specified in ARB regulations. If initial results show that the product does not meet the applicable VOC standards, the Executive Officer may perform additional testing to confirm the initial results.

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[1] Alternate test methods may be used, as provided in section 6.0

3.5.2 If the results obtained under section 3.5.1 show that the product does not meet the applicable VOC standards, the Executive Officer will request the product manufacturer or responsible party to supply product formulation data. The manufacturer or responsible party shall supply the requested information. Information submitted to the ARB Executive Officer may be claimed as confidential; such information will be handled in accordance with the confidentiality procedures specified in Title 17, California Code of Regulations, sections 91000 to 91022.

3.5.3 If the information supplied by the manufacturer or responsible party shows that the product does not meet the applicable VOC standards, then the Executive Officer will take appropriate enforcement action.

3.5.4 If the manufacturer or responsible party fails to provide formulation data as specified in section 3.5.2, the initial determination of VOC content under this section 3.5 shall determine if the product is in compliance with the applicable VOC standards. This determination may be used to establish a violation of ARB regulations.

3.6 ***Final Determination of VOC Content***. If a product's compliance status is not satisfactorily resolved under section 3.5, the Executive Officer will conduct further analyses and testing as necessary to verify the formulation data.

3.6.1 If the accuracy of the supplied formulation data is verified and the product sample is determined to meet the applicable VOC standards, then no enforcement action for violation of the VOC standards will be taken.

3.6.2 If the Executive Officer is unable to verify the accuracy of the supplied formulation data, then the Executive Officer will request the product manufacture or responsible party to supply information to explain the discrepancy.

3.6.3 If there exists a discrepancy that cannot be resolved between the results of Method 310 and the supplied formulation data, then the results of Method 310 shall take precedence over the supplied formulation data. The results of Method 310 shall then determine if the product is in compliance with the applicable VOC standards, and may be used to establish a violation of ARB regulations.

4.0 CALCULATION OF VOC CONTENT

4.1 *Aerosol Products*

For aerosol products, the percent VOC content shall be calculated using the following equation:

$$\text{PERCENT VOC} = \frac{WL(TV-A-H-EL) + WP - EP}{WL + WP} \times 100\%$$

Where[2]:

WL = weight (gm) of liquid product excluding container and packaging

TV = weight fraction of non-propellant total volatile material (U.S. EPA 24/24A, ASTM D2369-87)

A = weight fraction of ammonia (as NH4) in liquid (ASTM D1426-93) or U.S. EPA Method 300.7

H = weight fraction of water in liquid (ASTM D3792-86 or ASTM D4017-88)

EL = weight fraction of exempt compounds in liquid (U.S. EPA Method 8240, U.S. EPA Method 18, ASTM D859-88, NIOSH 1400)

WP = weight (gm) of propellant (ASTM D3074-72 [as modified and include ASTM D3064-89] or ASTM D3063-79 [as modified and include ASTM D3064-89])

EP = weight (gm) of exempt compounds in propellant (U.S. EPA Method 18)

4.2 ***Non-Aerosol Products***

For non-aerosol products, the percent VOC content shall be calculated using the following equation:

$$\text{PERCENT VOC} = (TV-A-H-EL) \times 100\%$$

5.0 METHOD PRECISION AND ACCURACY

The precision of Method 310 was evaluated using seven representative products with known volatile organic compound (VOC) contents ranging from 6.2 to 81.2 percent VOC by weight. Each sample was divided into six portions, and each portion was separately analyzed to determine the VOC content. Based on the results of this analysis, the 95 percent confidence interval for Method 310 is 3.0 percent by weight (Wt/Wt%).

6.0 ALTERNATE TEST METHODS

[2] Alternate test methods, as provided in 6.0, or appropriate approved methods from section 2.0 may be used.

Alternative test methods which are shown to accurately determine the concentration of VOCs or constituent components in antiperspirant/deodorants, consumer products, or aerosol coating products (or their emissions) may be used upon written approval of the Executive Officer.

Appendix A
PROPELLANT COLLECTION PROCEDURES

1.0 APPLICATION

The procedure applies to modify ASTM D3074-72 and D3063-79 to allow collection of the propellant for analysis and density measurement for metal aerosol containers and glass aerosol containers, respectively. These modified procedures also retain the aerosol standard terminology listed in ASTM D3064-89. The aerosol product container is pierced and the propellant is bled into an evacuated manifold. After the manifold reaches atmospheric pressure, approximately 1 liter of the propellant is collected in a clean, evacuated Tedlar bag. For density measurement the propellant is collected into an evacuated 250 ml glass dilution bulb that has been weighed to the nearest 0.1 mg. After filling, the dilution bulb is re-weighed to determine the density of the propellant. Alternately, density may be determined using a Density/Specific Gravity Meter. The Tedlar bag with the propellant aliquot is taken to the laboratory for analysis.

2.0 LIMITATIONS

Nitrogen analysis: Nitrogen may be used as a component of the propellant system. Ambient air is 78 percent nitrogen and may be present as a contaminate in the system prior to sample collection. This is eliminated by completely evacuating the propellant collection system and sweeping out any connecting lines to the Tedlar bag with product before starting sample collection. This procedure will eliminate or reduce nitrogen contamination to less than 0.1% by weight of the sample and the analysis of the propellant gas will be unaffected.

3.0 APPARATUS AND MATERIALS

3.1 Propellant Collection System[3]: See Figure 1. The system was built from 1/4" stainless steel and Teflon tubing. The vacuum pump is of bellows diaphragm design.

3.2 Tedlar Bags, 1 liter, equipped with slip valve and septum

3.3 Density Measurement

3.3.1 250 ml gas dilution bulb

3.3.2 or, an Density/Specific gravity meter meeting the following minimum specifications:

3.3.2(a). Measurement Method: Natural Oscillation Type

The metal piercing adapter is available from Mid-West Screw Products, Inc., 3523 North Kenton Ave., Chicago, IL 60641. Interim Part Number: 8013A-3/4 Longer SS. The gasket is available from Alltech Associate 2051 Waukegan road, Deerfield, IL 60015, part number 80-16. The glass aerosol adapter is available from Modern Machine Ship, Inc. P.O. Box 826, 123 N. Hazel Street, Danville, IL 61832.

3.3.2(b). Range: 0 - 3g/cm^3

3.3.2(c). Measurement Temperature Range: 4^oC ~ 70^0C.

3.3.2(d). Temperature Accuracy: +/- 0.02^0C (10^0C ~ 30^0C) and +/-0.05^0C (4^0C ~70^0C).

3.3.2(e). Temperature Control Accuracy: +/- 0.01^0C.

3.3.2(f). Measurement Time: 1- 4 minutes.

3.4 Gas tight syringe, 100 μl

3.5 Balance, capable of accurately weighing to 0.1 mg

3.6 Can Piercing Platform. See Figure 2 (metal cans) and Figure 3 (glass containers).

3.7 Platform Shaker, equivalent to Thermolyne M49125

4.0 PROCEDURE

4.1 Propellant Collection for Metal Aerosol Containers

4.1.1 Turn on vacuum pump, close valves and evacuate the system (see Figure 1).

4.1.2 Remove the valve actuator on the aerosol can and weigh can to the nearest 0.01 g. Invert the can into cork holding ring on the piercing apparatus, center and snug against the gasket. (Figure 2)

4.1.3 Connect Tedlar bag to output 2, evacuate bag and seal. Connect 250 ml glass dilution bulb to output 1, evacuate bulb and seal.

4.1.4 Slowly raise the hydraulic jack until the can is pierced. Record the pressure of the can.

4.1.5 Vent the can until the pressure is at about 25 psi. Collect the propellant in the Tedlar bag.

4.1.6 After the propellant is collected, close and remove the Tedlar bag and vent the remainder of the propellant.

4.1.7 Weigh the evacuated 250 ml bulb to the nearest 0.1 mg. Use gloves while handling the bulb. Connect the bulb to the tedlar bag and open to fill the bulb. Close the valves and re-weigh the dilution bulb, record the weight gain and calculate the propellant density in gm/l.

4.1.8 After the flow ceases from the can, it is removed from the assembly and allowed to vent overnight. The can may be placed on a platform shaker to vent the remainder of the propellant.

4.1.9 Reweigh can to the nearest 0.01 gm and record weight loss (total gms propellant). The can may now be opened for analysis of the liquid product.

4.2 Propellant Collection for Glass Aerosol Containers

4.2.1 Turn on vacuum pump, close valves and evacuate the system (see Figure 1).

4.2.2 Connect Tedlar bag to output 2, evacuate bag and seal. Connect 250 ml glass dilution bulb to output 1, evacuate bulb and seal.

4.2.3 The gauge assembly is prepressurized in order to minimize product expulsion and system contamination.

4.2.4 Remove actuator from valve of the aerosol glass container, and weigh container to the nearest 0.01gm.

4.2.5 With container in an inverted position place the valve onto the tapered adaptor. Bring the top plate down to the flat of the container and tighten the nuts. A cork ring may be required to stabilize the container.

4.2.6 Record pressure of container and vent until the pressure is approximately one-half of recorded pressure. Collect propellant sample into the tedlar bag.

4.2.7 After the propellant is collected, close and remove the tedlar bag and vent the remainder of the propellant.

4.2.8 Weigh the evacuated 250 ml bulb to the nearest 0.1 mg. Use gloves while handling the bulb. Connect the bulb to the Tedlar bag and open to fill the bulb. Close the valves and re-weigh the dilution bulb, record the weight gain and calculate the propellant density in gm/l.

4.2.9 Continue to vent container on the platform assembly overnight.

4.2.10 Remove container from platform and loosen valve assembly, do not remove valve assembly at this time.

4.2.11 Place container on a platform shaker to vent the remainder of the propellant.

4.2.12 Reweigh container and valve assembly to the nearest 0.01 gm and record weight loss (total gms propellant). The container may now be opened for analysis of the liquid product.

FIGURE 1

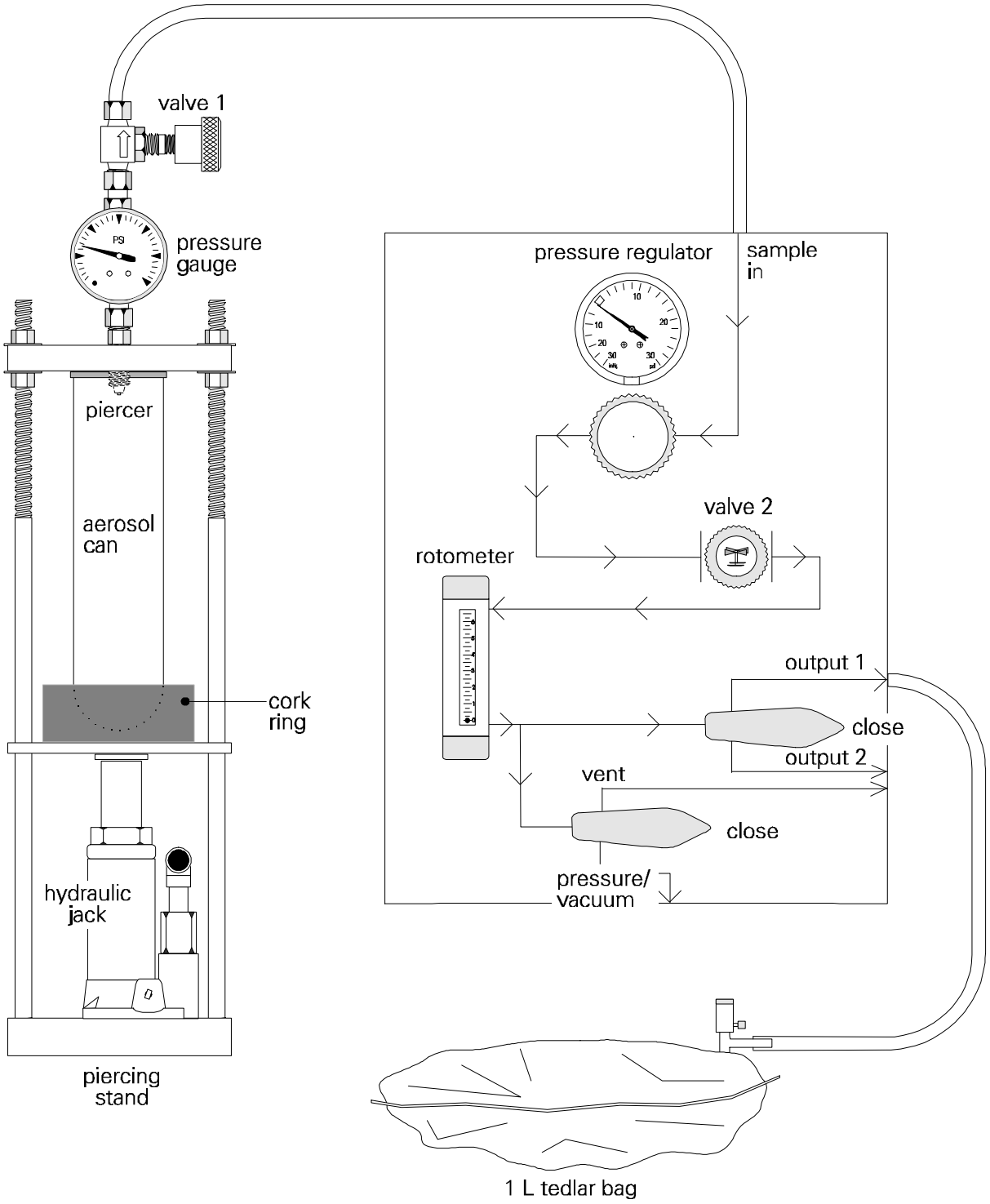
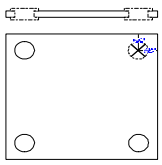
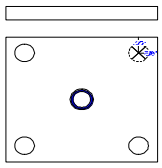

valve 1
pressure gauge
piercer
aerosol can
cork ring
hydraulic jack
piercing stand
pressure regulator
sample in
valve 2
rotometer
output 1
close
output 2
vent
close
pressure/ vacuum
1 L tedlar bag

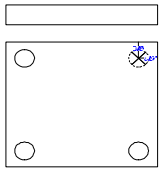
FIGURE 2



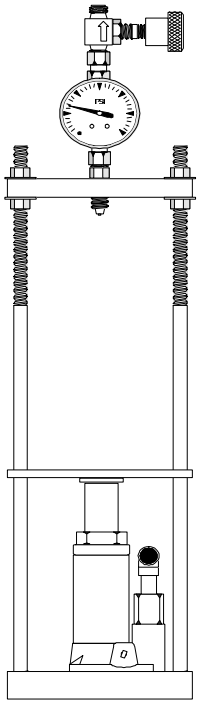
6" X 6" X 3/16" Steel Jack Plate
Center Holes 5/8" from edge
Drill 4 perimeter holes to allow
for a 1/2" bushing that works
with the smooth portion of the 1/2" rods
Tack weld the lift portion of the
hydraulic jack to the center of the plate
(weld while jack is fully extended as to
not damage it)



6" X 6" X 1/2" Aluminum Piercing Plate
Center holes 5/8" from edge
Drill 4 perimiter hole with 9/16" bit
Drill center holes with 7/16" bit
Tap center using 1/2 X 20 NF tap
Sample piercer is included to ensure
drill bit and tap size as center hole is
crucial to apparatus)



6" X 6" X 3/4" Aluminum Base Plate
Center holes 5/8" from edge
Drill 4 perimeter holes with 23/32" bit
Tap 4 perimeter holes with 1/2 X 13



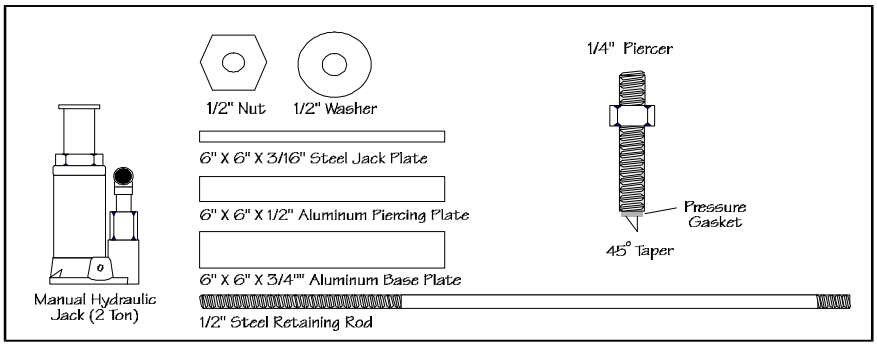


FIGURE 3